MEMORANDUM

TO: ICCR Coordinating Committee

FROM: ICCR Testing and Monitoring Protocol Workgroup (TMPWG)

RE: Typical Products of Incomplete Combustion (PICs) from industrial combustion sources that are also Hazardous Air Pollutants (HAP's).

DATE: November 7, 1997

The ICCR Coordinating Committee (CC) requested at the September CC Meeting that the ICCR Testing and Monitoring Protocol Workgroup (TMPWG) prepare a document that discusses typical products of incomplete combustion (PICs) that are included on the CAAA Hazardous Air Pollutant list. PICs are defined by the US EPA as follows:

> Products of Incomplete Combustion (PICs): Organic compounds formed by combustion. Usually generated in small amounts and sometimes toxic, PICs are heat altered versions of the material fed into the incinerator (e.g., charcoal is a PIC from burning wood).

There have been two presentations at ICCR Coordinating Committee meetings that have addressed combustion processes/conditions that can lead to the formation of PIC' s as follows:

> Chlorinated Dioxin and Furan Formation, Control and Monitoring, Gullet, Dr. Brian, and Seeker, Dr. Randy, Presented at the ICCR CC meeting, September 17, 1997.
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> Petroleum Environmental Research Forum (PERF) Project 92-19, "The Origin and Fate of Toxic Combustion Byproducts in Refinery Heaters: Research to Enable Efficient Compliance with the Clean Air Act," Seebold, James G.,et. al., Presented at the ICCR CC meeting July 22-23, 1997 by the Process Heater Work Group.

The information contained in these presentations and other references will be summarized and conclusions on HAP's/PIC's that are indicative of combustion practices and that are consistently detected in emissions from combustion sources will be drawn.

<u>Summary of HAP/PIC Formation Mechanisms in Combustion Process</u>

As discussed in the Dioxin/Furan Primer, fundamental research on the principles of organic combustion indicate that under good combustion conditions (i.e., high temperature and

available oxygen) the thermodynamic equilibrium levels of organics are negligible. In addition, under good combustion conditions the kinetics proceed rapidly to completion. However, in the "real world" of combustion optimum kinetic conditions are not readily and uniformly achieved which leads to the formation of HAPs/PICs.

In general, the efficiency of a combustion unit for completely utilizing fuel and waste feeds is governed by time, temperature and turbulence. Efficient combustion is achieved when all feeds to the combustion system reach an optimum temperature for a minimum residence time with sufficient turbulence to allow oxidation of all organic compounds to completely react to the products of combustion; water and carbon dioxide. There are a considerable number of operating practices and phenomena associated with combustion that lead to the formation of HAPs/PIC's. A detailed discussion of all these "failure" mechanisms is beyond the scope of this memorandum. However, for the sake of completeness, a list of some of these mechanisms include:

- Unburned fuel/waste due to channeling
- Quenches or cool zones in the combustion chamber
- Fuel rich zones or packets
- Low combustion temperature due to high excess air
- Insufficient air (oxygen) due to limited turbulence
- Changes to the combustion process due to load swings or feed changes

As discussed previously, the theoretical products of combustion are water and carbon dioxide. The mechanisms or phenomena identified above lead to the formation of PIC's, which can also be HAP's. One of the most prevalent PIC's generated in combustion processes is carbon monoxide. It is generally present in combustion process flue gases at part per million levels and is readily measured with existing technology. Carbon monoxide is often used as an excellent indicator of the efficiency of a combustion process.

There are other factors that can affect HAP/PIC emissions from combustion devices. If halogens (e.g., chlorine, bromine) are present in the fuel(s), then halogenated HAP's/PIC's can make up a significant portion of the total HAP/PIC emissions. Additionally, the type of control device utilized by the combustion unit can control some HAP's/PIC's formed in the combustion chamber. HAP's/PIC's can adhere to particulate matter or ash that is subsequently removed in downstream control dev ices (i.e., ESP, fabric filter). Additionally, wet scrubbing systems can sufficiently cool the flue gas stream to condense some HAP's/PIC's or water soluble species can be removed in these devices.

Conclusion - Typical HAP's/PIC's Resulting from Combustion Processes

Information on HAP emissions contained in the attached reference list was reviewed in an attempt to identify HAP's that are consistently detected in the flue gas from combustion units. Emphasis was placed on these constituents being present in the flue gas at detectable levels at

multiple sites and the relative levels of all HAP's/ PIC's detected or measured for in the flue gas. Typical HAP's/PIC's that can be utilized to evaluate the effectiveness of a combustion system include:

Acetaldehyde
Benzene
Formaldehyde
Naphthalene
Polycyclic Aromatic Hydrocarbons (PAH's)
Toluene
Xylenes

REFERENCES

Study of Hazardous Air Pollutant Emissions from Electric Utility Steam Generating Units -- Interim Final Report, United States Environmental Protection Agency, Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina, EPA-453/R-96-013a, October 1996.

Emissions of Organic Hazardous Air Pollutants from the Combustion of Pulverized Coal in a Small-Scale Combustor, Miller, C. Andrew, Srivastava, Ravi K., and Ryan, Jeffery V., Environmental Science Technology, Volume 28, Number 6, 1994, pp. 1150-1158.

Characterization of Air Toxics from an Oil-Fired Firetube Boiler, Miller, C. Andrew, Ryan, Jeffery V. and Lombardo, Tony, Journal of the Air & Waste Management association, Volume 46, 1996, pp. 742 - 748.

Chlorinated Dioxin and Furan Formation, Control and Monitoring, Gullet, Dr. Brian, and Seeker, Dr. Randy, Presented at the ICCR CC meeting, September 17, 1997.

Petroleum Environmental Research Forum (PERF) Project 92-19, "The Origin and Fate of Toxic Combustion Byproducts in Refinery Heaters: Research to Enable Efficient Compliance with the Clean Air Act," Seebold, James G., et. al., Presented at the ICCR CC meeting July 22-23, 1997 by the Process Heater Work Group.

HAP lists generated by the ICCR Testing and Monitoring Protocol Work Group for the ICCR Boiler Source Work Group.

HAP lists generated by the ICCR Testing and Monitoring Protocol Work Group for the ICCR Process Heater Source Work Group.

HAP lists generated by the ICCR Testing and Monitoring Protocol Work Group for the ICCR Internal Combustion Engine Source Work Group.

HAP lists generated by the ICCR Testing and Monitoring Protocol Work Group for the ICCR Combustion Turbine Source Work Group.